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Project HORIZONTAL Validation Report

Validation of a horizontal standard for the determination of adsorbable organically bound halogens (AOX) in soils, sludge and treated biowaste in a European Intercomparison Exercise

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Summary

Project HORIZONTAL is interdisciplinary aiming at a harmonisation and horizontal standardisation of test procedures, in particular for sludge, soils and biowastes. In the context of this standardization project, a series of draft technical specification were designed upon an extensive desk study, fine-tuned after expert consultations and finally validated in international intercomparisons exercise.

This report summarises the work performed within the validation study of the draft standard for the determination of adsorbable organically bound halogens (AOX) in soils, sludge and treated bio-waste. It further explains the underlying statistical concept for the calculation of reproducibility and repeatability from intercomparisons data. In addition all single values, results of the statistical evaluation as well as background information on the validation materials used are described and explained.

Abbreviations

Throughout this report the following abbreviations are used:

ANOVA	Analysis of variances
AOX	Adsorbable Organically Bound Halogens
CAS	Chemical Abstracts System
CEN	Comitteé Européen de Normalisation
DG	Directorate General
ECN	Energy Research Centre for the Netherlands
EU	European Union
IES	Institute for Environment and Sustainability
IT	Information Technology
ISO	International Organization for Standardisation
JRC	Joint Research Centre
MILC	Measure Interlaboratory Comparison
p	Number of labs
r	Repeatability limit
R	Reproducibility limit
s_r	Repeatability standard deviation
s_R	Reproducibility standard deviation
TC	Technical Committee

Table of Contents

Introduction to the validation project

Project HORIZONTAL is interdisciplinary aiming at a harmonisation and horizontal standardisation of test procedures, in particular for sludge, soils and biowastes. It was created as in response to the European Commission Mandate M 330 given to CEN, asking for the development and validation of those standards in support of forthcoming EU Directives, such as:

- The revision of the Sewage Sludge Directive 86/278/EEC.
- The Directive on the biological treatment of biodegradable waste.
- The initiative on a legal framework for soil monitoring in Europe.

This mandate explicitly considers standards for the entire analytical procedure (i.e., sampling, pre-treatment and analytical measurement methods for inorganic, organic, hygiene and biological parameters). These are grouped into classes according to their physical/chemical properties, which in turn determine the methods needed to quantify the potential impact on human and animal health, plant uptake, soil function and groundwater quality. As the materials generally feature a mixture of different types of contaminants, it is important to provide an integrated answer covering evaluation of all relevant pollutants.

In order to fulfil the requirements of the aforementioned mandate, the European Commissions Joint Research Centre (JRC) and its Directorate-General for Environment (DG ENV) together with the Technical Committees of the European Standardisation Committee (CEN TCs) concerned designed a pre-normative research initiative called Project HORIZONTAL and presented it to the Commission and the Environmental Authorities in the Member States.

After an extensive literature research and careful evaluation of the feasibility of a given horizontal standard, the standards were drafted and finally validated in a European laboratory intercomparison.

The underlying statistical concept, information about the materials used, details about the participants, measurement results obtained as well as the derived performance characteristics obtained for the determination of adsorbable organically bound halogens (AOX) are described hereafter.

1.1 Statistical concept underlying the validation

According to the requirements of the work package concerning data handling & interpretation of the project HORIZONTAL-ORG the respective validation intercomparisons have to be evaluated according to the principles laid down in ISO standard 5725-2:1994. In particular repeatability and reproducibility of the draft standard methods have to be determined. The determination of trueness would require the availability of independent reference values for the materials investigated. This, however, is not possible and was not requested in the frame of this work. In the following, the approach chosen is explained.

1.1.1 Introduction to the statistical model

The statistical model used in ISO 5725 for estimation of accuracy of a measurement method assumes that every test result is the sum of three components:

$$y = m + B + e$$

y: test result
m: general mean
B: laboratory component of bias under repeatability conditions
e: random error occurring in every measurement under repeatability conditions

In the workprogram the quantification of term *e* is explicitly asked for (i.e. repeatability and reproducibility). The repeatability variance is measured directly as the variance of the error term *e*, but the reproducibility depends on the sum of the repeatability variance and the between-laboratory variance:

$$\sigma_r = \sqrt{\mathrm{var}(e)}$$

$$\sigma_R = \sqrt{\sigma_L^2 + \sigma_r^2} \qquad \text{with} \qquad \sigma_L = \sqrt{\mathrm{var}(B)}$$

Using ANOVA techniques the different variances are calculated and separated for the evaluation.

1.1.2 Requirements for precision experiment

Layout of the experiment

A suite of 10 to 12 different materials (soil, sludge and biowaste) has been made available for the intercomparison exercise. For each parameter investigated, at least 10 to laboratories should be nominated to participate. The same laboratories should be used for different parameters as far as possible. Due to the complexity of analysis and the respective workload to the laboratories, it was decided to propose three materials for the validation of the AOX draft standard.

Each laboratory received two bottles of each material and was be requested to perform 6 independent analyses per material[1] (3 per bottle) using the respective draft standard methods. The 6 analyses per material should be carried out under repeatability conditions (i.e. same operator[2], same equipment, within a short period of time). As far as possible, also the different materials should be measured under repeatability conditions; however, changes of e.g. operator or equipment are permitted, but must be reported. Likewise, different materials can be analysed on different days if necessary.

Equipment used in the experiment needed to be checked prior to the experiment according to the requirements of the draft standard. The results of these checks have to be documented. Similarly, date and time of each measurement had to be recorded for verification of repeatability conditions.

An appropriate timeframe for the entire exercise has been set and was to be respected.

Recruitment of the laboratories

Each sub-workpackage leader of HORIZONTAL was asked to select the laboratories using the information from section 5.2 of ISO 5725-2:1994 and provide the signed questionnaires (see also Annex 1). The workpackage leaders were responsible for providing the laboratories with the draft standard method and explaining the context of this exercise.

Preparation and use of the materials

Materials used for the exercise were prepared according to the general requirements for reference materials as laid down in ISO Guide 34. Materials were accompanied by instructions for use.

Reporting of results

Online submissions of results using an internet-based IT platform as well as XLS-Spreadsheets were used. In case of online data submission, the participating laboratories received a unique and confidential login and password in due time, enabling them to enter their data in a structured form. For authentication purposes a signed printout had to be submitted by mail.

The online data submission included a detailed questionnaire for additional information on the measurements.

1.1.3 Statistical analysis

Statistical analysis of data followed the requirements of ISO 5725-2:1994 and ISO 5725-5:1998. Appropriate tests for the homogeneity of variance, detection of outliers and normal distribution were applied. Statistical evaluation was done using an Excel

[1] Independent analysis means analysis of independent test portions, applying the entire analytical scheme to this test portion, from e.g. extraction to quantification. For instance it does not mean replicate injections of aliquots into a GC-MS instrument.

[2] Operator in this context may also consist of a fixed team of persons, e.g. one person performing extraction, one clean-up, one quantification.

Macro, developed, tested and successfully applied in other occasion by ECN. Evaluation was executed jointly by JRC and ECN.

1.2 Validation exercise for AOX

1.2.1 Samples dispatched for the validation of AOX

After a preliminary rough screening, the following materials were used for the validation round of AOX.

- Compost 1 — A pollutant loaded compost material from Vienna
- Compost 2 — A pollutant loaded compost materia from Germany
- Sewage Sludge 1 — A mixed sewage sludge from Essen, Germany
- Sewage Sludge 2 — A mixed municipal WWTP sludge from North Rhine Westphalia, Germany
- Soil 4 — A sludge amended soil from Hohenheim, Germany
- Soil 5 — An agricultural soil from Reading, UK

A more detailed description of background concentrations can be found in Annex 2 to this report. The samples were dispatched simultaneously to all participants using a private courier service.

1.2.2 Draft standards to be followed

The draft standards to be followed could be downloaded following this link, which is situated on the website of the Project HORIZONTAL:

http://www.ecn.nl/docs/society/horizontal/AOX_standard_for_validation.pdf

1.2.3 Analytical program

Of each of the six materials 2 bottles had to be analyzed and each bottle had to analyze independently three times. As mentioned above analyses were to be done under repeatability conditions. Results were to be reported referring to DRY MATTER content. The choice, how to apply d.m. correction was free for each participant.

1.2.4 Timing and Submission of data

Dispatch of samples was done on the 18th of October 2006. For users of the Online data submission system (MILC), User Registration was possible from 14th of November 2006 with opening of the MILC Data Submission on 1st of December 2006. The deadline for submission of results has been set for AOX to the 12th of January 2007, but was extended to the end of the same months. After that no further submission was possible.

Alternatively the participants were allowed to submit data electronically as Excel sheet using simply Email.

All data were treated in a confidential way. Any presentation hereafter will refer only to numerical data and it will not be possible to identify the originating laboratory. Lab Codes displayed are NOT related to the order of laboratories hereafter.

In addition to the information provide a Helpdesk was implemented in order to give quick and individual response to the participants during and immediately after the validation study. In case of doubt and suspected transcription errors, further enquires were conducted by JRC.

1.2.5 Participants

The following table lists the participating organizations and entities in the validation exercise for the horizontal AOX standard;

- Austria
  - NUA Umweltanalytik GmbH
  - Porr Umwelttechnik GmbH
- Czech Republic
  - Central Institute for Supervising and Testing in Agriculture (UKZUZ)
- Denmark
  - Eurofins
- Germany
  - Federal Environmental Agency, Section III 3.4, Laboratory Methods for the Surveillance of Waste and Wastewater
  - Bundesanstalt fuer Materialforschung und -pruefung (BAM)
  - Reinhalteverband Großraum Salzburg
  - Emschergenossenschaft/Lippeverband
  - Hygiene-Institut des Ruhrgebiets
  - Landeshauptstadt Duesseldorf, Stadtentwaesserungsbetrieb
  - Staatliches Umweltamt
  - Ruhrverband Essen
  - Entsorgungsgesellschaft Krefel
  - Zantrallabor
  - Biolab Umweltanalysen GmbH

1.3 Summary results and derived performance characteristics

The result of the various statistical evaluation including outlier tests, calculation of repeatability and reproducibility standard deviation for AOX can be found in Annex 3 of this report. In addition, all data submitted by the participants as well as those considered for the calculation of the performance characteristics are listed in Annex 3 to this report.

Based on these calculations the following results were obtained in the validation round upon statistical evaluation according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table1).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures. The repeatability limit was calculated using the relationship: $r = f \cdot \sqrt{2} \cdot s_r$ with the critical range factor f = 2.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures. The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor f = 2.

Table 1 - Results of the interlaboratory comparison studies of the determination of adsorbable organically bound halogens (AOX) in treated biowaste, sludge and soil. All concentrations are expressed in mg/kg dm.

Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Total number of data
Compost 1	AOX	37.9	8.96%	25.9%	9.51	27.5	5	0	25
Compost 2	AOX	46.4	10.70%	25.3%	13.90	32.9	13	1	54
Sludge 1	AOX	215.0	9.21%	13.1%	55.40	78.9	15	1	67
Sludge 2	AOX	189.0	4.65%	8.2%	24.61	43.6	9	4	43
Soil 4	AOX	26.7	9.86%	34.2%	7.38	25.6	14	0	62
Soil 5	AOX	21.5	13.8%	31.7%	8.32	19.1	13	0	62

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of lab

1.4 Annexes

Annex 1: Model questionnaire to be filled by the participating laboratories

Annex 2: Report on the validation materials used

Annex 3: Statistical calculations

Annex 4: Data submitted

Annex 1:

Model questionnaire to be filled by the participating laboratories

Model questionnaire to be filled by the participating laboratories

Name of laboratory:
Contact person:
Contact details: email:
Phone:
Fax:
Mail address of lab:

Dispatch address of lab for shipment of samples (no PO boxes!):

Title of measurement method (copy attached):

Our laboratory is willing to participate in the precision experiment for this draft standard method.

Yes ☐ No ☐

As participant we understand that:

- All essential apparatus, chemicals and other requirements specified in the method must be available in our laboratory when the programme begins
- Specified timing requirements such as starting and finishing date of the programme must be rigidly met
- The method must be strictly adhered to
- Samples must be handled in accordance with instructions
- A qualified operator must perform the measurements

Having studied the method and having made a fair appraisal of our capabilities and facilities, we feel that we will be adequately prepared for cooperative testing of this method.

Comments:

……………………………………………………………………………………….

Signature Date

Annex 2:

Report on the validation materials used

Abstract

This report gives an overview on the available analytical information on the following raw materials to be used for the production of validation materials of the so-called Project HORIZONTAL:

- Four sludge materials from Düsseldorf, Germany,
- An agricultural soil material from Reading, United Kingdom;
- A compost material from Vienna, Austria;
- A compost material from Korschenbroich, Germany;
- A sludge-amended, agricultural soil from Pavia Province, Italy;
- A sludge-amended soil from Barcelona, Spain
- A sludge-amended soil from Essen, Germany
- A long-term sludge exposed soil from Hohenheim, Germany

List of Abbreviations

Throughout this report the following abbreviations are used.

AOX	absorbable organic halogens
C_{org}	organic carbon content
C_{total}	total carbon content
CAT	cation exchangeable
CDD	chlorinated dibenzodioxin
CDF	chlorinated dibenzofuran
DEHP	di(2-ethylhexyl)phthalate
DM	dry matter
EPA	Environment Protection Agency
EU	European Union
FM	fresh matter
Hp	hepta
Hx	hexa
IES	Institute for Environment and Sustainability
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
LAS	linear alkylsulfonates
LoD	limit of detection
LUA	Landesumweltamt
N_{total}	total nitrogen content
NH_4-N	Ammonium nitrogen
NO_3-N	Nitrate nitrogen
NP	nonylphenol
NRW	North Rhine Westphalia
O	octa
P	poly
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
Pe	penta
T	tetra
TEQ	toxicity equivalent
UBA	Umweltbundesamt
WHO	World Health Organization
WWTP	waste water treatment plant

1 Introduction

This report gives an overview on the available analytical information on the following raw materials to be used for the production of validation materials of the so-called Project HORIZONTAL:

- Four sludge materials from Düsseldorf, Germany,
- An agricultural soil material from Reading, United Kingdom;
- A compost material from Vienna, Austria;
- A compost material from Korschenbroich, Germany;
- A sludge-amended, agricultural soil from Pavia Province, Italy;
- A sludge-amended soil from Barcelona, Spain
- A sludge-amended soil from Essen, Germany
- A long-term sludge exposed soil from Hohenheim, Germany

The following analytical information was gathered partly before and during the sampling of the raw materials, to be used for the production of the HORIZONTAL validation materials. The material were sampled by IES and shipped to IRMM in the course of the year 2005. The information gathered was then completed by various analytical screenings for PAHs and PCBs done by the Institute for Reference Materials and Measurements, Geel, Belgium, for phthalates done by UBA, Berlin, Germany, for PBDE done by IIQAB-CSIC, Barcelona, Spain, for trace elements and some selected major and minor elements by the Institute for Environment and Sustainability, Ispra, Italy.

The work compiled hereafter is based on the numerous additional efforts of the scientists working at various members of the consortium Project HORIZONTAL-Org and contributing organisations.

This work is gratefully acknowledged.

2 Overview on property values

2.1 Sludge materials from Düsseldorf, Germany

The various sewage sludge materials originate from various installations in the North Rhine Westphalia and were produced and sampled by staff from the Landesumweltamt (LUA) NRW under the responsibility from Dr. K. Furtmann.

In total, four sludge materials (Sludge A and D from a major municipal WWTP, Sludge B from a municipal WWTP with industrial input, and Sludge C from a municipal WWTP with high PCB-Content,) were obtained and will be blended to two final materials. Before sampling the following analytical data for a typical sample were received.

Table 1 – Analytical data obtained on an average sludge sample in LUA NRW (with courtesy of K. Furtmann, LUA, Düsseldorf)

Parameter	*Concentration*
PCB	120 ug/kg
DEHP	110 mg/kg
PAH	5 mg/kg (EPA)
PCDD/F	15 ng TE/kg
PBDE	400 ug/kg
NP	40 mg/kg
LAS	3 g/kg
AOX	300 mg/kg

Subsequent screening led to the information displayed hereafter. It should be stressed that the data were obtained as SCREENING information on the UNTREATED or partially treated raw materials. Therefore, the final target values, which are relevant for the validation intercomparison can be different.

Table 2 – Analytical data obtained on a first screening on the sludge samples from LUA NRW

	Sewage sludge A Dusseldorf	*sewage sludge D Dusseldorf*
PCB (ng/g)		
28	62	35
52	101	65
101	31	38
118	49	40
153	30	33
105	24	11
138	46	38
156	<1	<1
180	34	23
170	23	19
PAH (ng/g)		
Naphtalene	34	381
Acenaphtylene	15	43
Acenaphthene	81	108
Fluorene	94	1167
Phenantrene		3440
Anthracene	22	344
Flouranthene	316	4817
Pyrene	235	3011
Benz(a)anthracene	473	791
Chrysene	691	1078
Benz(b)fluoranthene	538	1688
Benz(k)fluoranthene	228	635
Benz(a)pyrene	383	1114
Indeno(1,2,3-c,d)pyrene	92	229
Dibenzo(a,h)anthracene	71	70
Benzo(g,h,i)perylene	80	185

Table 3 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Sludge D (1)		0.135		41.474	3.85
Sludge B (2)	0.538	0.034		30.634	5.47
Sludge A (3)	0.184	0.037		31.399	1.46
Sludge C (4)		0.354	1.528	6.678	2.29

Table 4 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Sludge 2 (B)
Tetra-BDE-47	55.4
Penta-BDE-100	9.59
Penta-BDE-99	69.4
Hexa-BDE-154	5.91
Hexa-BDE-153	7.72
Hepta-BDE-183	5.09
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	9.70
Deca-BDE-209	2216
TOTAL	2379

Table 5 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena, IES, Ispra, Spain). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Sludge 1 (D)	2.65	29.0	53.3	359	1231	33.8	78.4	4.38	< 0.05	23.2	786
Sludge 2 (B)	1.19	31.1	62.6	202	278	29.9	72.2	2.51	< 0.05	11.8	625
Sludge 3 (A)	1.68	36.0	62.1	332	847	41.6	119	4.51	< 0.05	11.6	1237
Sludge 4 (C)	5.63	19.8	116	273	726	51.1	473	6.18	< 0.05	44.4	2015

Table 6 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Sludge 1 (D)	21.54	5.8	8.44	0.99	10.3	1.01	4367	<15	50448
Sludge 2 (B)	10.67	3.66	6.92	0.46	14.91	0.77	5217	<15	57633
Sludge 3 (A)	7.31	6.63	6.84	0.35	12.87	0.68	3733	<15	60369
Sludge 4 (C)	43.79	9.65	5.27	1.63	5.22	1.07	5628	<15	23945

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Sludge 1 (D)	0.3	2403	101	1002	350	15	1944	132
Sludge 2 (B)	0.31	315	97	879	172	12	514	180
Sludge 3 (A)	0.31	1281	153	1567	265	16	1440	168
Sludge 4 (C)	0.55	231	628	2625	371	81	1101	244

2.2 *Agricultural soil material from Reading, United Kingdom*

The material was proposed by the University of Reading (S. Nortcliff) and was sampled from a site called "*Frogmore Farm*" which was featured in the "*Metals*" Report for HORIZONTAL. This site is close to Reading with soils developed on flintyloamy periglacial materials over Chalk, has a long and well documented history of sludge application. The focus of the work of Nortcliff *et al.* undertook at this site and the monitoring and control at the site (by Thames Water and the subsequent subsidiary bodies dealing with sludge application to soil) was on metals (and metal loads), with no analysis or indeed any form of investigation in to organics in the broadest sense.

The analytical information produced in the context of the screening of the raw material is displayed below.

Table 7 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 3 (Reading)		0.032		0.119	6.69

Table 8 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 3 (Reading)	0.15	7.06	27.9	13.8	152	9.01	26.7	3.00	< 0.05	25.8	93.1

Table 9 – Analytical data obtained on a first screening on the sludge-amended soil from Reading (courtesy of IRMM)

Parameter	*Concentration*
PCB	**ng/g**
28	<1
52	<1
101	<1
118	<1
153	<1
105	<1
138	<1
156	<1
180	<1
170	<1
PAH	**ng/g**
Naphtalene	<10
Acenaphtylene	21
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	<10
Flouranthene	818
Pyrene	776
Benz(a)anthracene	565

Parameter	*Concentration*
Chrysene	608
Benz(b)fluoranthene	824
Benz(k)fluoranthene	329
Benz(a)pyrene	799
Indeno(1,2,3-c,d)pyrene	779
Dibenzo(a,h)anthracene	118
Benzo(g,h,i)perylene	394

Table 10 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 3 (Reading)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	1.03
Hexa-BDE-154	0.03
Hexa-BDE-153	nq
Hepta-BDE-183	nq
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	272
TOTAL	273

Table 11 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 3 (Reading)	0.15	7.06	27.9	13.8	152	9.01	26.7	3.00	< 0.05	25.8	93.1

Table 12 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 3 (Reading)	79.36	4.77	1.12	0.96	1.94	0.17	4107	443	2102

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 3 (Reading)	0.42	13	45	69	69	69	216	92

Table 13 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg** µg/g*
Soil 3 (Reading)	0.12

2.3 Compost from Vienna, Austria

The fresh compost material was obtained from the Austrian Federal Environment Agency (UBA, Vienna), which had used a sub-batch of the raw material for national intercomparson. The remainder of the material was stored at 4°C until shipment to IRMM for further processing. The following analytical information was provided by UBA Austria and completed with various screenings.

Table 14 – Analytical data on compost material received from UBA Austria Inorganic and sum parameters

Parameter	*Unit*	*Sample fraction used*	*Observed mean*
B CAT	mg/l F.M.	Fresh sample, <10mm	6.1
K CAT	mg/l F.M.	Fresh sample, <10mm	2624
Mg CAT	mg/l F.M.	Fresh sample, <10mm	242
P CAT	mg/l F.M.	Fresh sample, <10mm	49
B CAT	% D.M.	Fresh sample, <10mm	0.0017
K CAT	% D.M.	Fresh sample, <10mm	0.72
Mg CAT	% D.M.	Fresh sample, <10mm	0.07
P CAT	% D.M.	Fresh sample, <10mm	0.01
NO3-N	mg/kg F.M.	Fresh sample, <10mm	3.5
NH4-N	mg/kg F.M.	Fresh sample, <10mm	230
Ctotal	% D.M.	<45°dry, milled	29
Corg	% D.M.	<45°dry, milled	27
Ntotal	% D.M.	<45°dry, milled	1.7
P	mg/kg D.M.	<45°dry, milled	2596
K	mg/kg D.M.	<45°dry, milled	11019
K	% D.M.	<45°dry, milled	1.10
B	mg/kg D.M.	<45°dry, milled	60
Cd	mg/kg D.M.	<45°dry, milled	0.46
Cr	mg/kg D.M.	<45°dry, milled	25
Cu	mg/kg D.M.	<45°dry, milled	46
Hg	mg/kg D.M.	<45°dry, milled	0.20
Ni	mg/kg D.M.	<45°dry, milled	18
Pb	mg/kg D.M.	<45°dry, milled	45
Zn	mg/kg D.M.	<45°dry, milled	198
Ca	mg/kg D.M.	<45°dry, milled	68776
Ca	% D.M.	<45°dry, milled	6.9
Mo	mg/kg D.M.	<45°dry, milled	0.8
S	mg/kg D.M.	<45°dry, milled	2137
Fe	mg/kg D.M.	<45°dry, milled	9959
Mn	mg/kg D.M.	<45°dry, milled	418
Na	mg/kg D.M.	<45°dry, milled	742
Co	mg/kg D.M.	<45°dry, milled	4.1
AOX	mg/kg D.M.	<30° dry, milled	62

Table 15 – Analytical data on compost material received from UBA Austria Polycyclic aromatic hydrocarbons

PAH	*Unit*	*Result*
Naphthaline	µg/kg DM	9.3
Acenaphthylene	µg/kg DM	8.6
Acenaphthene	µg/kg DM	5
Fluorene	µg/kg DM	8.0
Phenanthrene	µg/kg DM	89
Anthracene	µg/kg DM	27
Fluoranthene	µg/kg DM	487
Pyrene	µg/kg DM	380

PAH	*Unit*	*Result*
Benzo(a)anthracene	µg/kg DM	278
Chrysene	µg/kg DM	317
Benzo(b)fluoranthene	µg/kg DM	365
Benzo(k)fluoranthene	µg/kg DM	193
Benz(a)pyrene	µg/kg DM	320
Indeno(1,2,3-c,d)pyrene	µg/kg DM	233
Dibenz(a,h)anthracene	µg/kg DM	67
Benzo(g,h,i)perylene	µg/kg DM	225
Sum EPA	µg/kg DM	3013
Sum EPA	mg/kg DM	3.0

Table 16 – Analytical data on compost material received from UBA Austria Sum PCDDs and PCBs

Parameter			
Dioxine	TEQ (ITEF)	ng/kg DM	7.3
PCB	TEQ (WHO)	ng/kg DM	3.5
	Σ Ballschmiter	mg/kg DM	0.05

Table 17 – Analytical data on compost material obtained by screening in IRMM

Parameter	*Result in ng/g*
PCB	
28	2
52	2
101	4
118	3
153	10
105	1
138	8
156	1
180	5
170	<1
PAH	
Naphtalene	<10
Acenaphtylene	<10
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	26
Fluoranthene	611
Pyrene	510
Benz(a)anthracene	888
Chrysene	957
Benz(b)fluoranthene	1531
Benz(k)fluoranthene	547
Benz(a)pyrene	1101
Indeno(1,2,3-c,d)pyrene	416
Dibenzo(a,h)anthracene	81
Benzo(g,h,i)perylene	295

Table 18 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Compost 1 (Vienna)
Tetra-BDE-47	4.02
Penta-BDE-100	0.19
Penta-BDE-99	2.59
Hexa-BDE-154	nq
Hexa-BDE-153	0.23
Hepta-BDE-183	0.04
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	1.44
Deca-BDE-209	17.4
TOTAL	25.9

Table 19 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Compost 1 (Vienna)		0.058		1.426	5.57

Table 20 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Compost 1 (Vienna)	0.39	7.36	31.9	41.0	365	12.7	49.5	0.04	0.79	0.13	208

Table 21 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Compost 1 (Vienna)	20.63	4.31	6.17	4.26	1.99	2.49	1602	<15	10521

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Compost 1 (Vienna)	0.35	3496	81	375	79	55	653	60

Table 22 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Compost 1 (Vienna)	0.17

2.4 Agricultural soil, sludge amended soil from Pavia, Italy

This sludge-amended soil material was obtained during a monitoring campaign, which aimed at a generic description of the over-all soil quality in Pavia Province, Italy. The material, which was collected from the upper horizon, originates from a small farm called "*Cascina Novello*". During the characterisation of the site, the following analytical information was obtained on a pooled sample of a sub-area of the farm of 20 X 20 m^2.

Table 23 – Analytical data on Pavia soil

Parameter	*Result*
Al	7.13 Wgt%
As	22.4 mg/kg
Cd	0.79 mg/kg
Cr	59 mg/kg
Cu	30.8 mg/kg
Hg	0.08 mg/kg
Ni	34.4 mg/kg
Pb	24.6 mg/kg
Zn	95 mg/kg
C	0.91 Wgt %
2,3,7,8-TCDD	0.047 pg/g
1,2,3,7,8-PeCDD	0.15 pg/g
1,2,3,4,7,8-HxCDD	0.19 pg/g
1,2,3,6,7,8-HxCDD	1.5 pg/g
1,2,3,7,8,9-HxCDD	0.74 pg/g
1,2,3,4,6,7,8-HpCDD	26 pg/g
OCDD	382 pg/g
2,3,7,8-TCDF	0.68 pg/g
1,2,3,7,8-PeCDF	0.53 pg/g
2,3,4,7,8-PeCDF	0.71 pg/g
1,2,3,4,7,8-HxDF	1.00 pg/g
1,2,3,6,7,8-HxDF	0.66 pg/g
2,3,4,6,7,8-HxDF	1.6 pg/g
1,2,3,7,8,9-HxDF	0.27 pg/g
1,2,3,4,6,7,8-HpDF	12 pg/g
1,2,3,4,7,8,9-HpDF	0.68 pg/g
OCDF	33 pg/g
I-TEQ	2.0 pg/g
WHO-TEQ	1.7 pg/g

In addition, the screening performed at IRMM did not reveal significant quantities of PCBs and PAHs, which were all below the LoDs (1 ng/g for PCBs and 10 ng/g for PAHs, respectively).

Table 24 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g TM	µg/g TM	µg/g TM	µg/g TM	Wgt. %
Soil 5 (Pavia)		0.005		0.011	1.54

Table 25 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 5 (Pavia)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	0.39
Hexa-BDE-154	nq
Hexa-BDE-153	nq
Hepta-BDE-183	0.08
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	670
TOTAL	671

Table 26 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 5 (Pavia)	0.33	18.4	57.3	22.5	426	30.5	20.6	2.00	< 0.05	38.1	87.8

Table 27 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 5 (Pavia)	69.39	12.9	1.45	2.24	4.25	1.16	6118	255	1789

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 5 (Pavia)	1.84	62	38	108	55	66	597	110

Table 28 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Soil 5 (Pavia)	0.06

2.5 Sludge-amended-soil from Barcelona, Spain

The sludge-amended soil material from Barcelona sampled upon indication from the Barcelo'- Group in Barcelona.

Table 29 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 2 (Lleida T.)		0.015		0.183	11.38

Table 30 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 2 (Lleida T.)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	1.59
Hexa-BDE-154	0.45
Hexa-BDE-153	nq
Hepta-BDE-183	0.48
Octa-BDE-196	1.60
Octa-BDE-197	nq
Octa-BDE-203	nq
Deca-BDE-209	1000
TOTAL	1004

Table 31 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	**Co**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Tl**	**V**	**Zn**
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 2 (Lleida T.)	0.59	14.1	32.7	53.6	405	18.6	18.4	2.24	< 0.05	31.8	111

Table 32 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	SiO2 (%)	Al2O3 (%)	CaO (%)	K2O (%)	Fe2O3 (%)	MgO (%)	TiO2 (PPM)	S (PPM)	P2O5 (PPM)
Soil 2 (Lleida T.)	44.43	10.67	14.29	2.53	3.44	2.04	4116	780	3396

Sample	Na2O (%)	Cl (PPM)	Pb (PPM)	Zn (PPM)	Cu (PPM)	Ni (PPM)	Mn (PPM)	Cr (PPM)
Soil 2 (Lleida T.)	0.64	65	26	125	59	17	547	65

Table 33 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	**Hg** *µg/g*
Soil 2 (Lleida T.)	0.10

2.6 Sludge amended soil from Essen, Germany

The German sludge-amended soil from Essen, which was provided as the three sludge materials by LUA NRW, did not feature significant concentrations of the PCB congeners 28, 52, 101, 118, 153, 105, 138, 156, 180, 170, but had detectable amounts of some PAHs.

Table 34 – Analytical screening data on the German sludge-amended soil.

Parameter	*Concentration (ng/g)*
Naphtalene	<10
Acenaphtylene	<10
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	<10
Fluoranthene	28
Pyrene	20
Benz(a)anthracene	24
Chrysene	47
Benz(b)fluoranthene	76
Benz(k)fluoranthene	20
Benz(a)pyrene	35
Indeno(1,2,3-c,d)pyrene	35
Dibenzo(a,h)anthracene	10
Benzo(g,h,i)perylene	26

Table 35 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 4 (Essen)		0.011		0.302	0.55

Table 36 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 4 (Essen)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	nq
Hexa-BDE-154	nq
Hexa-BDE-153	nq
Hepta-BDE-183	nq
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	1.28
Deca-BDE-209	19.1
TOTAL	20.3

Table 37 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Tl	V	Zn
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 4 (Essen)	0.52	5.45	26.1	8.05	320	4.03	27.3	2.73	< 0.05	29.5	78.1

Table 38 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	SiO2 (%)	Al2O3 (%)	CaO (%)	K2O (%)	Fe2O3 (%)	MgO (%)	TiO2 (PPM)	S (PPM)	P2O5 (PPM)
Soil 4 (Essen)	79.47	4.42	0.85	0.6	0.86	0.07	2163	189	2019

Sample	Na2O (%)	Cl (PPM)	Pb (PPM)	Zn (PPM)	Cu (PPM)	Ni (PPM)	Mn (PPM)	Cr (PPM)
Soil 4 (Essen)	0.45	19	42	87	683	60	462	61

Table 39 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	Hg µg/g
Soil 4 (Essen)	0.04

2.7 Long-term sludge exposed soil from Hohenheim-Stuttgart, Germany

Similarly, an additional sludge exposed soil was sampled at the University of Hohenheim, Stuttgart, were a test soil was long-term exposed to elevated concentrations of sewage sludge.

Table 40 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	DBP	DCHP	DEHP	Water
	µg/g TM	µg/g TM	µg/g TM	µg/g TM	Wgt. %
Soil 1 (Stuttgart)		0.045		0.263	17.65

Table 41 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 1 (Stuttgart)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	2.30
Hexa-BDE-154	0.06
Hexa-BDE-153	0.04
Hepta-BDE-183	0.04
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	498
TOTAL	500

Table 42 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 1 (Stuttgart)	0.69	12.7	36.1	26.2	504	18.3	25.2	2.62	< 0.05	26.6	142

Table 43 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 1 (Stuttgart)	71.94	10.06	1.33	1.86	3.66	0.88	7874	275	3571

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 1 (Stuttgart)	1.23	50	47	212	85	69	991	129

Table 44 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Soil 1 (Stuttgart)	1.77

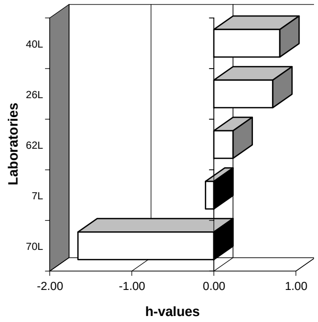
Annex 3:

Statistical calculations

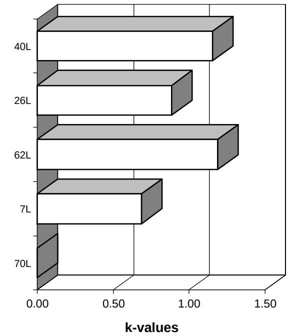
Sample: **Compost 1**

Element: **AOX**

Mandel's h statistics
(Compost 1 - AOX)



Mandel's k statistics
(Compost 1 - AOX)



Unit: mg Cl /kç

Mandel's k statistics (Compost 1 - AOX)
Mandel's h statistics (Compost 1 - AOX)

Compost 1 - AOX -- Mean PARM = 37.92 [mg Cl /kg]

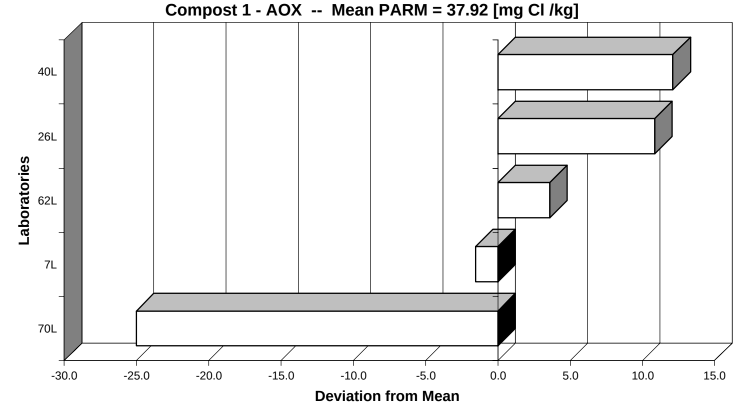
	General calc.parm.
T1=	1.07300E+03
T2=	4.77315E+04
T3=	25
T4=	145
T5=	2.3060E+02
n=	variabel
p=	5
N-table=	*5*

Mandel's statistics — End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark \vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
70L	12.9000	-	1	!	-1.66			Fail	12.9000 -			1		-25.02
7L	36.3833	2.334	6		-0.10	0.69			36.3833	2.3336		6	5	-1.53
62L	41.5000	4.037	6		0.24	1.19	Fail		41.5000	4.0373		6	5	3.58
26L	48.7667	2.999	6		0.72	0.88	Fail		48.7667	2.9992		6	5	10.85
40L	50.0333	3.922	6		0.81	1.15	Fail		50.0333	3.9216		6	5	12.12
Tot.gem	37.917	3.323	mg Cl /kg	*1%-level:*	1.72	(1.6)		5	*37.9167*	()		5	4	
Tot.std=	15.046	0.807		*5%-level:*	1.57	(1.44)								

RESULTS:	**Mean =**	**37.91667**	*mg Cl /kg*			
Repeatability variance	**S2r =**	11.52985				
Repeatability std.	**Sr =**	**3.39556**	-->	8.96%	**r =**	9.5076
Between lab variance	**S2L =**	85.01279				
Reproducibility var.	**S2R =**	96.54264				
Reproducibility std.	**SR =**	**9.82561**	-->	25.91%	**R =**	27.5117
Remarks:	**none**					

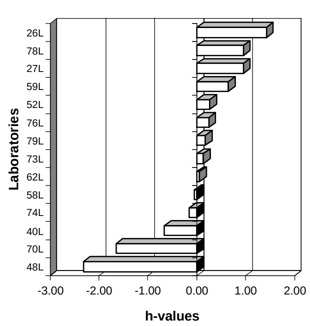
Compost 1 - AOX -- Mean PARM = 37.92 [mg Cl /kg]



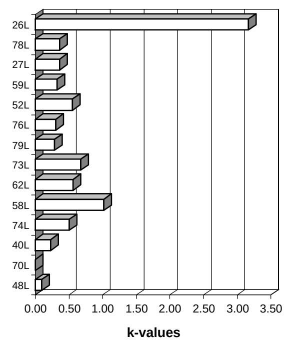
Sample: **Compost 2**

Element: **AOX**

Mandel's h statistics (Compost 2 - AOX)



Mandel's k statistics (Compost 2 - AOX)



Unit: mg Cl /kg

Mandel's k statistics (Compost 2 - AOX)
Mandel's h statistics (Compost 2 - AOX)

Compost 2 - AOX -- Mean PARM = 46.45 [mg Cl /kg]

	General calc.parm.
T1=	2.52400E+03
T2=	1.23863E+05
T3=	54
T4=	258
T5=	1.0099E+03
n=	variabel
p=	13
N-table=	*4*

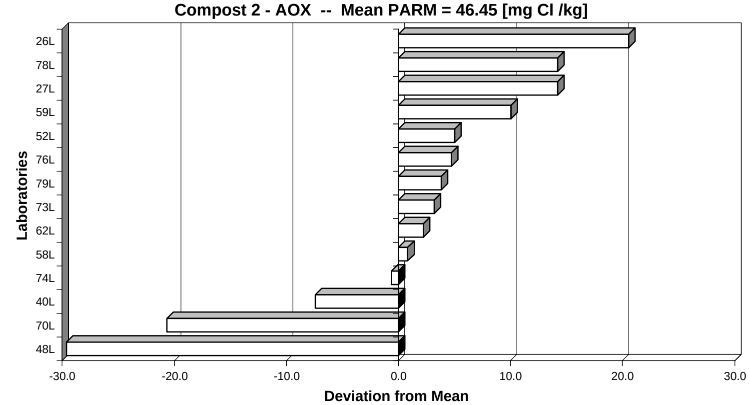
Mandel's statistics

End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
48L	16.8450	0.947	4	!!	-2.32	0.10		Fail		16.8450	0.9472		4	3	-29.60
70L	25.8000	-	1		-1.65			Fail		25.8000 -			1		-20.65
40L	39.0167	2.221	6		-0.66	0.23				39.0167	2.2212		6	5	-7.43
74L	45.8000	4.891	4		-0.16	0.50				45.8000	4.8915		4	3	-0.65
58L	47.2750	9.884	4		-0.05	1.02				47.2750	9.8838		4	3	0.83
62L	48.6667	5.465	6		0.06	0.56				48.6667	5.4650		6	5	2.22
73L	49.6667	6.532	6		0.13	0.67				49.6667	6.5320		6	5	3.22
79L	50.2500	2.745	4		0.17	0.28				50.2500	2.7453		4	3	3.80
76L	51.1840	2.996	5		0.24	0.31				51.1840	2.9959		5	4	4.74
52L	51.4667	5.348	6		0.26	0.55				51.4667	5.3481		6	5	5.02
59L	56.5000	3.109	4		0.64	0.32				56.5000	3.1091		4	3	10.05
27L	60.6750	3.500	2		0.95	0.36				60.6750	3.5002		2	1	14.23
78L	60.6750	3.500	2		0.95	0.36				60.6750	3.5002		2	1	14.23
26L	67.0050	30.713	6		1.42	3.17	!!	Fail	-	-	,26L	-	-		20.56
Tot.gem	47.916	6.296 mg Cl /kg		*1%-level:*	2.30	(1.86)			13	*46.4477*	(26L)		13	12	
Tot.std=	13.401	7.677		*5%-level:*	1.85	(1.58)			1						

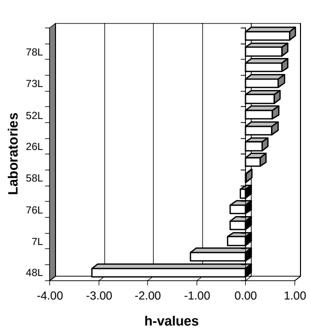
RESULTS:	**Mean =**	**46.44774**	*mg Cl /kg*			
Repeatability variance	**S2r =**	24.63175				
Repeatability std.	**Sr =**	**4.96304**	-->	10.69%	**r =**	13.8965
Between lab variance	**S2L =**	113.64443				
Reproducibility var.	**S2R =**	138.27618				
Reproducibility std.	**SR =**	**11.75909**	-->	25.32%	**R =**	32.9254
Remarks:	**1 Lab rejected! (26L)**					

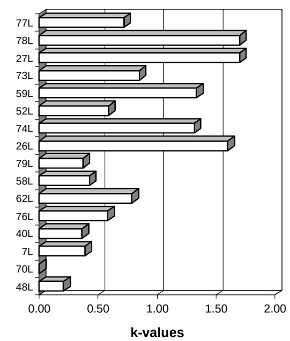
Compost 2 - AOX -- Mean PARM = 46.45 [mg Cl /kg]



Sample: **Sludge 1**

Element: **AOX**





Unit: mg Cl /kg

Mandel's k statistics (Sludge 1 - AOX)
Mandel's h statistics (Sludge 1 - AOX)

Sludge 1 - AOX -- Mean PARM = 214.9 [mg Cl /kg]

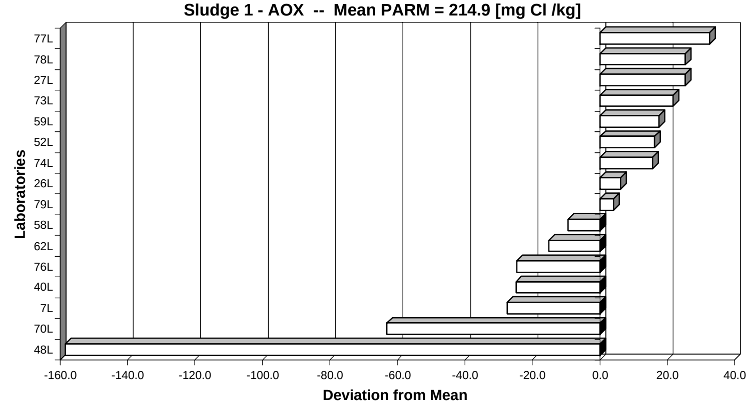
	General calc.parm.
T1=	1.43761E+04
T2=	3.11507E+06
T3=	67
T4=	339
T5=	2.0377E+04
n=	variabel
p=	15
N-table=	*4*

Mandel's statistics — End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*AvX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
48L	56.4725	4.276	4	**!!**	-3.14	0.21			Fail	-	-	,48L -	-		-158.43
70L	151.7000	-	1		-1.13				Fail	151.7000	-		1		-63.20
7L	187.5000	8.019	6		-0.37	0.39				187.5000	8.0187		6	5	-27.40
40L	190.0000	7.483	6		-0.32	0.36				190.0000	7.4833		6	5	-24.90
76L	190.3333	11.978	6		-0.31	0.58				190.3333	11.9778		6	5	-24.57
62L	199.8333	16.216	6		-0.11	0.79				199.8333	16.2162		6	5	-15.07
58L	205.5000	8.813	4		0.01	0.43				205.5000	8.8129		4	3	-9.40
79L	219.0000	7.703	4		0.30	0.37				219.0000	7.7028		4	3	4.10
26L	221.0000	33.008	6		0.34	1.60	**!**			221.0000	33.0078		6	5	6.10
74L	230.5000	27.111	4		0.54	1.31		Fail		230.5000	27.1109		4	3	15.60
52L	231.0167	12.143	6		0.55	0.59		Fail		231.0167	12.1431		6	5	16.12
59L	232.5000	27.538	4		0.58	1.33		Fail		232.5000	27.5379		4	3	17.60
73L	236.6667	17.512	6		0.67	0.85		Fail		236.6667	17.5119		6	5	21.77
27L	240.2133	35.050	3		0.75	1.70		Fail		240.2133	35.0497		3	2	25.31
78L	240.2133	35.050	3		0.75	1.70		Fail		240.2133	35.0497		3	2	25.31
77L	247.5000	14.849	2		0.90	0.72		Fail		247.5000	14.8492		2	1	32.60
Tot.gem	204.997	17.783 mg Cl /kg		*1%-level:*	2.33	(1.87)			15	*214.8984*		(48L)	15	14	
Tot.std=	47.257	10.865		*5%-level:*	1.86	(1.59)			1						

RESULTS:	**Mean =**	**214.89844**	*mg Cl /kg*			
Repeatability variance	**S2r =**	391.87037				
Repeatability std.	**Sr =**	**19.79572**	-->	9.21%	**r =**	55.4280
Between lab variance	**S2L =**	402.58438				
Reproducibility var.	**S2R =**	794.45475				
Reproducibility std.	**SR =**	**28.18607**	-->	13.12%	**R =**	78.9210
Remarks:	**1 Lab rejected! (48L)**					

Sludge 1 - AOX -- Mean PARM = 214.9 [mg Cl /kg]



Unit: mg Cl /kg

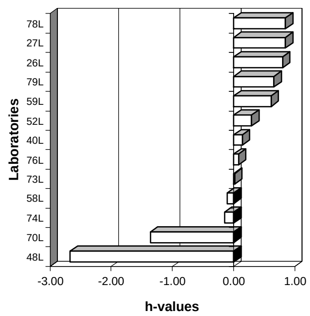
Mandel's k statistics (Sludge 2 - AOX)
Mandel's h statistics (Sludge 2 - AOX)

Sludge 2 - AOX -- Mean PARM = 188.9 [mg Cl /kg]

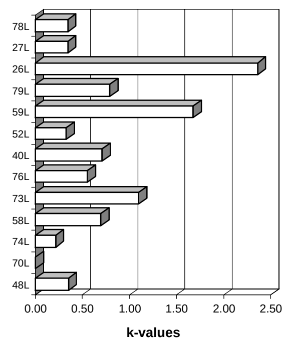
Sample: **Sludge 2**

Element: **AOX**

Mandel's h statistics (Sludge 2 - AOX)



Mandel's k statistics (Sludge 2 - AOX)



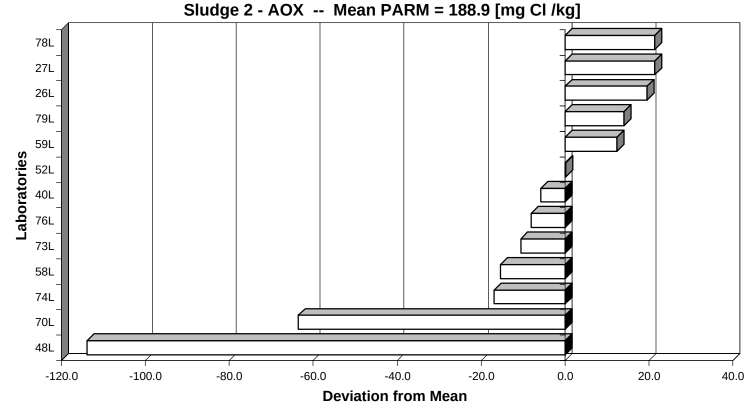
	General calc.parm.
T1=	8.01542E+03
T2=	1.50100E+06
T3=	43
T4=	219
T5=	2.6245E+03
n=	variabel
p=	9
N-table=	*4*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*AvX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
48L	75.0975	4.728	4	!!	-2.67	0.35			Fail	-	-	,48L -	-		-113.82
70L	125.4000	-	1		-1.36				Fail	-	-	,70L -	-		-63.52
74L	172.0000	2.915	5		-0.15	0.22				172.0000	2.9155		5	4	-16.92
58L	173.5000	9.327	4		-0.11	0.69				173.5000	9.3274		4	3	-15.42
73L	178.3333	14.720	6		0.02	1.10				178.3333	14.7196		6	5	-10.59
76L	180.8333	7.414	6		0.08	0.55				180.8333	7.4140		6	5	-8.09
40L	183.1667	9.496	6		0.14	0.71				183.1667	9.4956		6	5	-5.75
52L	189.0333	4.391	6		0.29	0.33				189.0333	4.3907		6	5	0.11
59L	201.2500	22.500	4		0.61	1.68	!	Fail		-	-	,59L -	-		12.33
79L	203.0000	10.614	4		0.66	0.79		Fail		203.0000	10.6145		4	3	14.08
26L	208.4767	31.678	6		0.80	2.36	!!	Fail		-	-	,26L -	-		19.56
27L	210.2033	4.640	3		0.84	0.35		Fail		210.2033	4.6404		3	2	21.28
78L	210.2033	4.640	3		0.84	0.35		Fail		210.2033	4.6404		3	2	21.28
Tot.gem	177.731	10.589 mg Cl /kg		*1%-level:*	2.27	(1.85)			9	*188.9193*		(26L ,70L ,48L ,59L)	9	8	
Tot.std=	38.445	8.629		*5%-level:*	1.84	(1.58)			4						

RESULTS:	**Mean =**	**188.91926**	*mg Cl /kg*			
Repeatability variance	**S2r =**	77.19191				
Repeatability std.	**Sr =**	**8.78589**	-->	4.65%	**r =**	24.6005
Between lab variance	**S2L =**	165.33691				
Reproducibility var.	**S2R =**	242.52882				
Reproducibility std.	**SR =**	**15.57334**	-->	8.24%	**R =**	43.6053
Remarks:	**4 Labs rejected! (26L ,70L ,48L ,59L)**					

Sludge 2 - AOX -- Mean PARM = 188.9 [mg Cl /kg]



Unit: mg Cl /kç

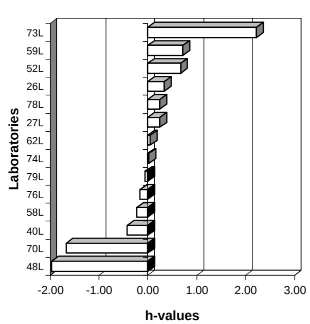
Mandel's k statistics (Soil 4 - AOX)
Mandel's h statistics (Soil 4 - AOX)

Soil 4 - AOX -- Mean PARM = 26.75 [mg Cl /kg]

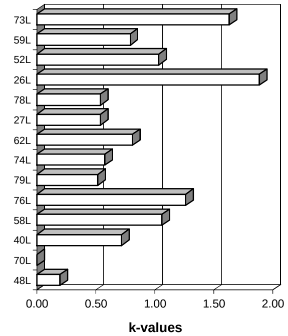
Sample: **Soil 4**

Element: **AOX**

Mandel's h statistics
(Soil 4 - AOX)



Mandel's k statistics
(Soil 4 - AOX)



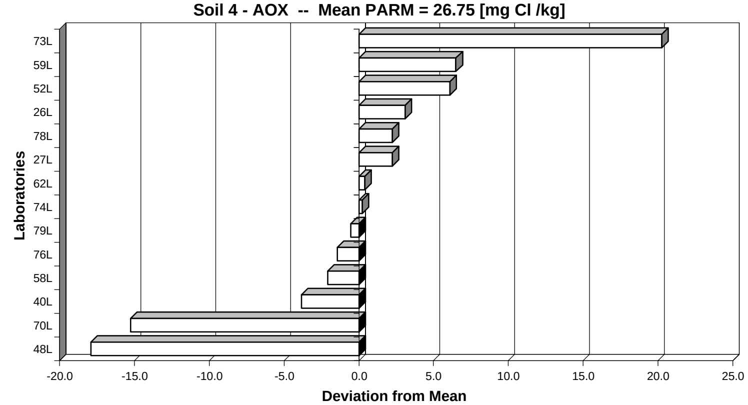
	General calc.parm.
T1=	1.74444E+03
T2=	5.35308E+04
T3=	62
T4=	314
T5=	3.3360E+02
n=	variabel
p=	14
N-table=	*4*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
48L	8.8350	0.473	4	!	-1.96	0.20			Fail	8.8350	0.4729		4	3	-17.91
70L	11.5000	-	1		-1.67				Fail	11.5000	-		1		-15.25
40L	22.9000	1.717	6		-0.42	0.72			Fail	22.9000	1.7170		6	5	-3.85
58L	24.6500	2.537	4		-0.23	1.06				24.6500	2.5371		4	3	-2.10
76L	25.3000	3.018	6		-0.16	1.26				25.3000	3.0179		6	5	-1.45
79L	26.2000	1.236	4		-0.06	0.52				26.2000	1.2356		4	3	-0.55
74L	26.9800	1.375	5		0.03	0.57				26.9800	1.3755		5	4	0.23
62L	27.1667	1.941	6		0.05	0.81				27.1667	1.9408		6	5	0.42
27L	28.9850	1.294	2		0.25	0.54				28.9850	1.2940		2	1	2.24
78L	28.9850	1.294	2		0.25	0.54				28.9850	1.2940		2	1	2.24
26L	29.8433	4.512	6		0.34	1.88	!!	Fail		29.8433	4.5118		6	5	3.10
52L	32.8500	2.469	6		0.67	1.03		Fail		32.8500	2.4688		6	5	6.10
59L	33.2500	1.893	4		0.71	0.79		Fail		33.2500	1.8930		4	3	6.50
73L	47.0000	3.899	6	!	2.22	1.63	!	Fail		47.0000	3.8987		6	5	20.25
Tot.gem	26.746	2.127 mg Cl /kg		*1%-level:*	2.30	(1.86)			14	*26.7461*	()		14	13	
Tot.std=	9.133	1.142		*5%-level:*	1.85	(1.58)									

RESULTS:	**Mean =**	**26.74607**	*mg Cl /kg*			
Repeatability variance	**S2r =**	6.94998				
Repeatability std.	**Sr =**	**2.63628**	-->	9.86%	**r =**	7.3816
Between lab variance	**S2L =**	76.55353				
Reproducibility var.	**S2R =**	83.50351				
Reproducibility std.	**SR =**	**9.13803**	-->	34.17%	**R =**	25.5865
Remarks:	**none**					

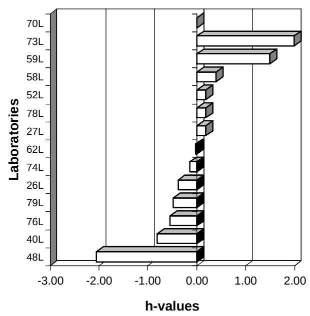
Soil 4 - AOX -- Mean PARM = 26.75 [mg Cl /kg]

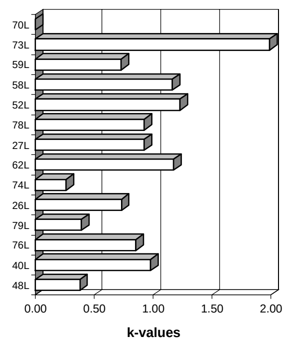


	Mandel's h statistics (Soil 5 - AOX)	Mandel's k statistics (Soil 5 - AOX)

Sample: **Soil 5**

Element: **AOX**





Unit: mg Cl /kç

Mandel's k statistics (Soil 5 - AOX)
Mandel's h statistics (Soil 5 - AOX)

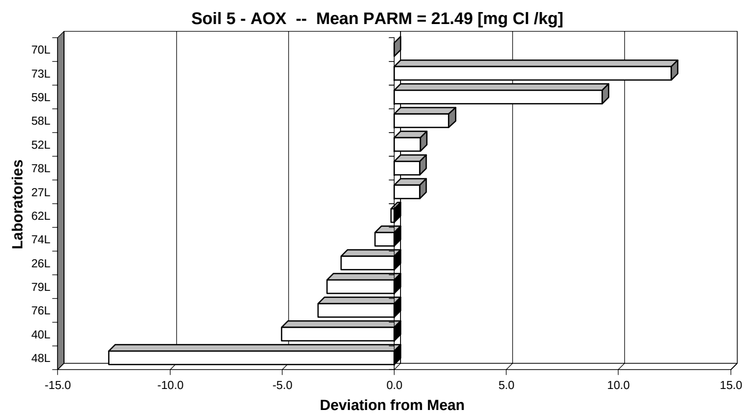
Soil 5 - AOX -- Mean PARM = 21.49 [mg Cl /kg]

	General calc.parm.
T1=	1.33111E+03
T2=	3.08159E+04
T3=	62
T4=	324
T5=	4.3288E+02
n=	variabel
p=	13
N-table=	*5*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*		*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*		*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
48L	8.7525	1.072		4	!	-2.05	0.38			Fail		8.7525	1.0721		4	3	-12.73
40L	16.4667	2.769		6		-0.81	0.98			Fail		16.4667	2.7689		6	5	-5.02
76L	18.1000	2.423		6		-0.55	0.85			Fail		18.1000	2.4232		6	5	-3.39
79L	18.5000	1.117		4		-0.48	0.39			Fail		18.5000	1.1165		4	3	-2.99
26L	19.1200	2.073		6		-0.38	0.73					19.1200	2.0728		6	5	-2.37
74L	20.6333	0.742		6		-0.14	0.26					20.6333	0.7421		6	5	-0.85
62L	21.3333	3.327		6		-0.02	1.17					21.3333	3.3267		6	5	-0.15
27L	22.6200	2.616		2		0.18	0.92					22.6200	2.6163		2	1	1.13
78L	22.6200	2.616		2		0.18	0.92					22.6200	2.6163		2	1	1.13
52L	22.6667	3.482		6		0.19	1.23					22.6667	3.4823		6	5	1.18
58L	23.9250	3.293		4		0.39	1.16					23.9250	3.2928		4	3	2.44
59L	30.7500	2.062		4		1.49	0.73		Fail			30.7500	2.0616		4	3	9.26
73L	33.8333	5.636		6	!	1.99	1.99	!!	Fail			33.8333	5.6362		6	5	12.35
70L	-	-		-					Fail		-	-		-	-		#VALUE!
Tot.gem	21.486	2.556	mg Cl /kg		*1%-level:*	2.27	(1.76)				13	*21.4862*	()		13	12	
Tot.std=	6.207	1.278			*5%-level:*	1.84	(1.51)										

RESULTS:	**Mean =**	**21.48622**	*mg Cl /kg*			
Repeatability variance	**S2r =**	8.83438				
Repeatability std.	**Sr =**	**2.97227**	-->	13.83%	**r =**	8.3224
Between lab variance	**S2L =**	37.54478				
Reproducibility var.	**S2R =**	46.37916				
Reproducibility std.	**SR =**	**6.81022**	-->	31.70%	**R =**	19.0686
Remarks:	**none**					



Annex 4:

Raw data submitted

Sample:	Compost 1
Element:	AOX
LAB	PARM
26L	47.93
26L	47.93
26L	50.88
26L	45.28
26L	53.63
26L	46.95
40L	52.500
40L	46.800
40L	50.000
40L	56.100
40L	49.600
40L	45.200
62L	38.000
62L	41.000
62L	47.000
62L	36.000
62L	43.000
62L	44.000
70L	12.900
7L	35.100
7L	34.400
7L	35.900
7L	36.600
7L	35.400
7L	40.900

Sample:	Compost 2
Element:	AOX
LAB	PARM
27L	63.150
27L	58.200
40L	37.200
40L	41.600
40L	38.900
40L	41.900
40L	37.000
40L	37.500
62L	44.000
62L	45.000
62L	50.000
62L	43.000
62L	55.000
62L	55.000
26L	108.54
26L	44.69
26L	47.05
26L	102.84
26L	39.58
26L	59.33
52L	45.100
52L	54.500
52L	46.000
52L	51.700
52L	52.100
52L	59.400
58L	58.100
58L	53.200
58L	38.400
58L	39.400
70L	25.800
73L	54.000
73L	42.000
73L	41.000
73L	54.000
73L	56.000
73L	51.000
48L	17.570
48L	15.800
48L	16.290
48L	17.720
74L	46.300
74L	52.500
74L	42.800
74L	41.600
59L	53.000
59L	58.000
59L	55.000
59L	60.000
76L	49.66
76L	52.92
76L	55.59
76L	48.38
76L	49.37
78L	63.15
78L	58.2
79L	49.5
79L	54.1
79L	47.6
79L	49.8

Sample:	Sewage Sludge 1
Element:	AOX
LAB	PARM
7L	175.000
7L	186.000
7L	191.000
7L	192.000
7L	183.000
7L	198.000
27L	202.910
27L	272.460
27L	245.270
40L	190.000
40L	187.000
40L	195.000
40L	201.000
40L	188.000
40L	179.000
62L	175.000
62L	197.000
62L	191.000
62L	204.000
62L	210.000
62L	222.000
26L	197.43
26L	204.99
26L	197.43
26L	279.54
26L	241.23
26L	205.38
52L	216.800
52L	223.900
52L	238.200
52L	231.400
52L	224.900
52L	250.900
58L	203.000
58L	216.000
58L	195.000
58L	208.000
70L	151.700
73L	230.000
73L	260.000
73L	250.000
73L	240.000
73L	230.000
73L	210.000
48L	62.000
48L	52.030
48L	57.340
48L	54.520
74L	244.000
74L	262.000
74L	205.000
74L	211.000
59L	260.000
59L	200.000
59L	250.000
59L	220.000
76L	181.000
76L	194.000
76L	200.000
76L	176.000
76L	184.000
76L	207.000
77L	258.000
77L	237.000
78L	202.91
78L	272.46
78L	245.27
79L	209
79L	224
79L	217
79L	226

Sample:	Sewage Sludge 2
Element:	AOX
LAB	PARM
27L	204.910
27L	212.130
27L	213.570
40L	170.000
40L	179.000
40L	183.000
40L	192.000
40L	196.000
40L	179.000
26L	270.31
26L	200.67
26L	189.37
26L	189.37
26L	188.78
26L	212.36
52L	195.900
52L	188.300
52L	191.300
52L	189.200
52L	182.900
52L	186.600
58L	163.000
58L	176.000
58L	170.000
58L	185.000
70L	125.400
73L	170.000
73L	200.000
73L	190.000
73L	170.000
73L	180.000
73L	160.000
48L	68.310
48L	76.390
48L	76.390
48L	79.300
74L	168.000
74L	175.000
74L	170.000
74L	174.000
74L	173.000
59L	175.000
59L	190.000
59L	220.000
59L	220.000
76L	173.00
76L	183.00
76L	190.00
76L	171.00
76L	182.00
76L	186.00
78L	204.91
78L	212.13
78L	213.57
79L	193.00
79L	200.00
79L	218.00
79L	201.00

Sample:	Soil 4
Element:	AOX
LAB	PARM
27L	28.070
27L	29.900
40L	24.500
40L	20.500
40L	23.800
40L	24.800
40L	21.900
40L	21.900
62L	26
62L	27
62L	31
62L	26
62L	26
62L	27
26L	26.23
26L	27.01
26L	28.78
26L	26.42
26L	33.3
26L	37.32
52L	35.300
52L	35.400
52L	33.900
52L	29.500
52L	30.500
52L	32.500
58L	24.500
58L	27.900
58L	21.700
58L	24.500
70L	11.500
73L	52.000
73L	44.000
73L	49.000
73L	50.000
73L	45.000
73L	42.000
48L	8.230
48L	9.380
48L	8.810
48L	8.920
74L	28.300
74L	28.000
74L	24.800
74L	26.800
74L	27.000
59L	32.000
59L	32.000
59L	33.000
59L	36.000
76L	22.9
76L	23.5
76L	30.1
76L	22.8
76L	24.6
76L	27.9
78L	28.07
78L	29.9
79L	27.0
79L	27.4
79L	25.7
79L	24.7

Sample:	Soil 5
Element:	AOX
LAB	PARM
27L	20.770
27L	24.470
40L	16.200
40L	16.300
40L	15.900
40L	21.800
40L	14.100
40L	14.500
62L	18
62L	20
62L	25
62L	19
62L	20
62L	26
26L	21.9
26L	20.33
26L	20.53
26L	17.58
26L	17.68
26L	16.7
52L	23.700
52L	20.700
52L	24.800
52L	21.600
52L	17.600
52L	27.600
58L	25.500
58L	21.500
58L	20.900
58L	27.800
73L	38.000
73L	33.000
73L	38.000
73L	36.000
73L	35.000
73L	23.000
48L	8.060
48L	9.110
48L	10.100
48L	7.740
74L	19.700
74L	19.900
74L	21.400
74L	21.500
74L	20.700
74L	20.600
59L	31.000
59L	28.000
59L	31.000
59L	33.000
76L	14.6
76L	18.2
76L	20
76L	15.9
76L	19
76L	20.9
78L	20.77
78L	24.47
79L	17.2
79L	18.0
79L	19.1
79L	19.7

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Abstract
Project HORIZONTAL is interdisciplinary aiming at a harmonisation and horizontal standardisation of test procedures, in particular for sludge, soils and biowastes. In the context of this standardization project, a series of draft technical specification were designed upon an extensive desk study, fine-tuned after expert consultations and finally validated in international intercomparisons exercise.
This report summarises the work performed within the validation study of the draft standard for the determination of adsorbable organically bound halogens (AOX) in soils, sludge and treated bio-waste. It further explains the underlying statistical concept for the calculation of reproducibility and repeatability from intercomparisons data. In addition all single values, results of the statistical evaluation as well as background information on the validation materials used are described and explained.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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